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Zur Lichtabsorption der Komplexe von Aminobenzolsulfosäuren.

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(Eingegangen im Januar 1949).

1. Einleitung.

Den Komplexen von Aminobenzolsulfosäuren schreibt Pfeiffer (1) eine betainartige Struktur zu (Vgl. Abb. 2, Form. a und Abb. 5, Form. c) U. E. wird diese Behauptung bei den Komplexen von Metanil- und Sulfanilsäure aus sterischen Gründen zutreffen. Die Metalle mit unaufgefüllten äusseren Elektronenschalen werden aber mit Orthanilsäure innerkomplexe Salze bilden. (Abb. 2, Form. b). Um dies zu beantworten wurden die Extinktionskurven der Komplexe von Orthanil- und Sulfanilsäure im Wasser bei Zimmertemperatur ausgemessen (2).

Bezüglich der experimentellen Einrichtung und der Messmethode verweisen wir auf früheren Arbeiten (3). Die Komplexe wurden nach Literaturangaben (4) hergestellt. Da auch die neuen Verbindungen ähnlicher Weise leicht zu erhalten sind, sehen wir von der Wiedergabe der Darstellungsvorschriften ab. Die Reinheit der Komplexe, bzw. die Konzentration der Lösungen wurden analytisch kontrolliert.

2. Zur Konstitution der Komplexe.

Bei den Alkali- und Erdalkali-Verbindungen findet eine elektrostatische Bindung zwischen Sulfogruppe und Metallion statt. So dissoziieren diese Komplexe im Wasser elektrolytisch. (1). Bei den komplexbildenden Metallen, mit unaufgefüllten äusseren Elektronenschalen, von der o-, bzw. p-Stellung der Amino- und Sulfogruppen abhängig u. E. entstehen innerkomplexe Salze (Abb. 2, Form. b, bzw. Abb. 5, Form. c). Demgegenüber schreibt Pfeiffer (1) beiden Verbindungsreihen betainartige Struktur zu. Bei den Komplexen der Orthanilsäure findet eine semipolare Bindung zwischen dem

Metallion und Stickstoffatom der Aminogruppe statt. Bei den Orthanilsäure-Komplexen der zweiwertigen Metalle sind die Liganden planar angeordnet, demzufolge können zwei Wassermoleküle in trans-Stellung festgehalten werden. Die Sulfanilsäure-Komplexe der zwei- und dreiwertigen Metalle sind koordinativ ungesättigt und können daher ihre freien Koordinationsstellen mit Wassermolekülen auffüllen. Auch die Sauerstoffatome der Sulfogruppe können mit ihren einsamen Elektronen Wassermoleküle binden.

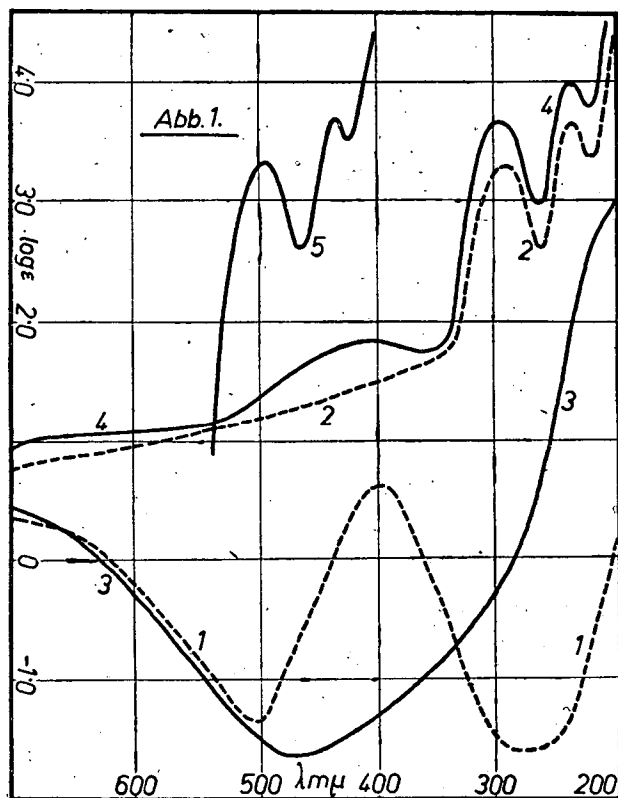


Abb. 1. Kurve 1: $\text{Ni}(\text{ClO}_4)_2 \cdot \text{K}$. 2: Co -orphanilat. K. 3: $\text{Fe}(\text{ClO}_4)_3 \cdot \text{K}$. 4: Cu -orphanilat. K. 5: Orthanilsäure.

3. Zum Mechanismus der Lichtabsorption.

Die Aminobensolsulfosäuren haben sowohl im Grund- als in dem Anregungszustand mehrere, miteinander in Resonanz stehende Grenzstrukturen (5). Der Benzolring und die Aminogruppe bedingen die Mesomerie. Die Sulfogruppe beteiligt sich in der Mesomerie in keiner merkbarer Weise (5).

Wegen der semipolaren Bindung zwischen Stickstoffatom und Metallionen werden in den Komplexen die Grenzformen b (Abb. 2) und c (Abb. 5) vorherrschen. Das Beibehalten der selektiven Absorption der Liganden in ihren Komplexen spricht für die Mesomeriefähigkeit der Aminogruppe.

Der beinahe gleiche Verlauf der Extinktionskurven von Orthanilsäure (Abb. 1, K. 5) und Sulfanilsäure (Abb. 4, K. 1) und ihrer Alkali- und Erdalkali-Komplexe (Abb. 3, K. 1—3, bzw. Abb. 4, K. 2—4) weist darauf hin, dass ihre Extinktionskurven additiver Art aus der selektiven Absorption ihrer Ausgangsstoffe zusammengesetzt sind. Dies spricht für die Dissoziation ihrer Komplexe im Wasser.

In der Lichtabsorption der Komplexe mit koordinativer Bindung beteiligen sich die Liganden, die eigenen Elektronen des Zentralions und die koordinativen Bindungselektronen (6).

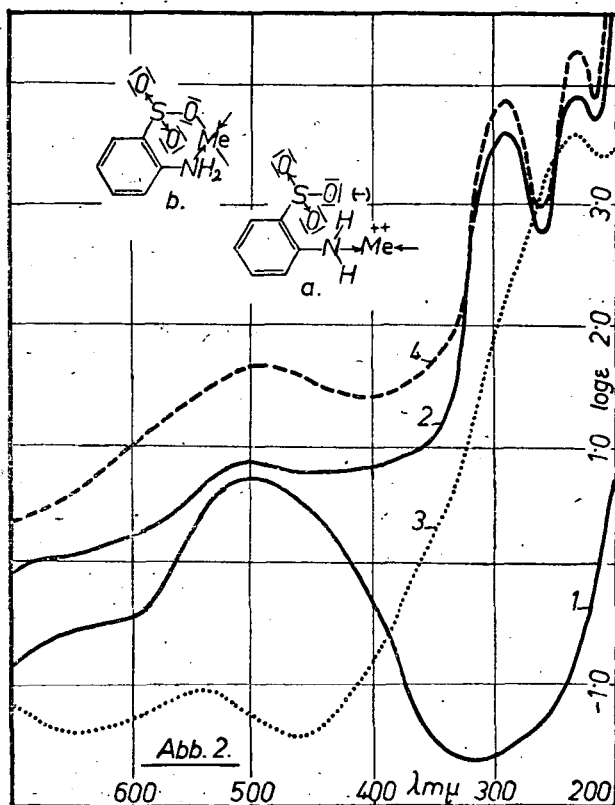


Abb. 2. Kurve 1: $\text{Co}(\text{ClO}_4)_3$. K. 2: Co-orphanilat. K. 3: $\text{Fe}(\text{ClO}_4)_3$. K. 4: Fe-orphanilat. a: Betainartige Struktur des Orphanil-Komplexes. b: Innerkomplexe Struktur des Orphanil-Komplexes.

Da in ihren Komplexen die Lage der Banden von Orphanil- und Sulfanilsäure beibehalten wird, (Vgl. Abb. 1—5), ändert die Komplexbildung kaum deren Elektronenanordnung. Nur die Übergangswahrscheinlichkeit wird geändert, worauf die Extinktionszunahme hinweist. Die Extinktion von Orphanil- und Sulfanilsäure wird von den einzelnen Metallionen ganz spezifisch geändert.

Ein Vergleich der Kurven der Orphanil- und Sulfanilsäure-Komplexe, sowie der Perchloraten der entsprechenden Metallionen (Abb. 1, K. 1 und 3, Abb. 2, K. 1 und 3) zeigt folgendes:

Bei den Orthanilsäure-Komplexen der gefärbten Ionen: Cu, Co, Ni und Fe wird die Bandenstruktur des Metallions beinahe voll-

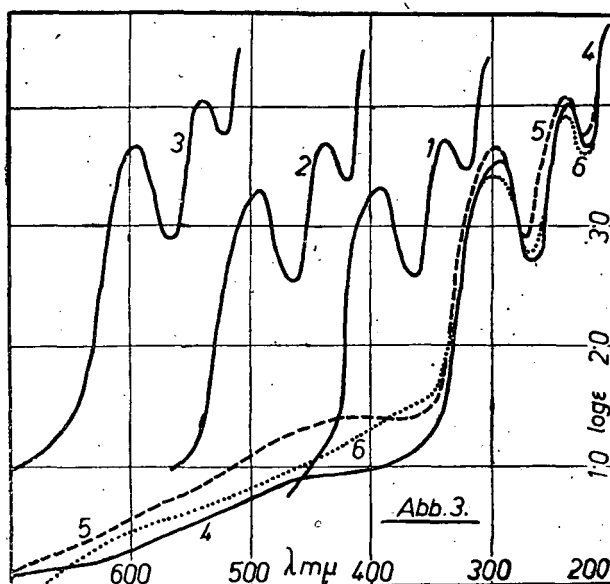


Abb. 3. Kurve 1: Na-orthanilat, K. 2: K-orthanilat, K. 3: Ba-orthanilat, K. 4: Mg-orthanilat, K. 5: Cd-orthanilat, K. 6: Zn-orthanilat.

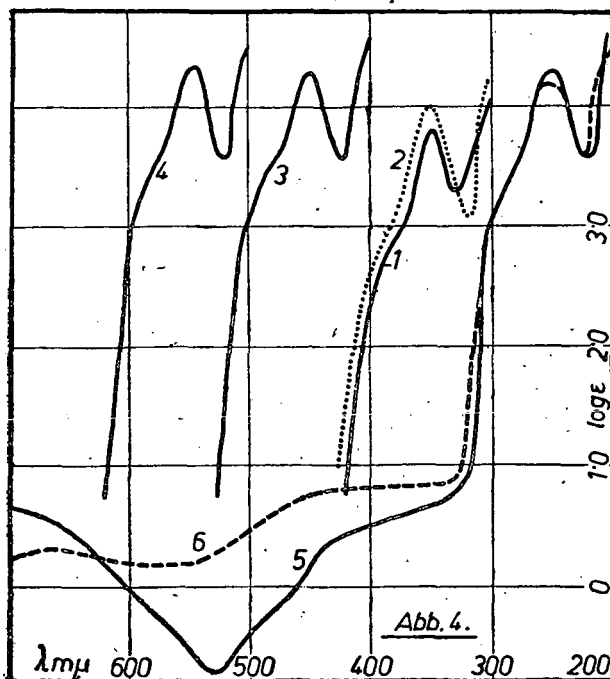


Abb. 4. Kurve 1: Sulfanilsäure, K. 2: K- und Na-sulfanilat, K. 3: Mg-sulfanilat, K. 4: Ba-sulfanilat, K. 5: Cu-sulfanilat, K. 6: Ni-sulfanilat.

ständig verwischt (Abb. 1, K. 2 und 4, Abb. 2, K. 2 und 4). Dabei nimmt die Extinktion im Sichtbaren und an der Grenze desselben stark zu. Bei den betainartigen Komplexen von Sulfanilsäure mit den erwehnten Metallionen, wird die Bandenstruktur der Zentralionen schwächer verwischt (Abb. 4, K. 5 und 6, Abb. 5, K. 4) Somit übt die freie Ladung bei den betainartigen Komplexen eine schwächere Wirkung auf die selektive Absorption des Zentralions aus, als die Ringbildung bei den innerkomplexen Verbindungen von Orthanilsäure. Dies kann durch die starke (durch die, in die wahre koordinative Bindung übergehende) Bindung der innerkomplexen Verbindungen bzw, durch die Ringbildung verursachte

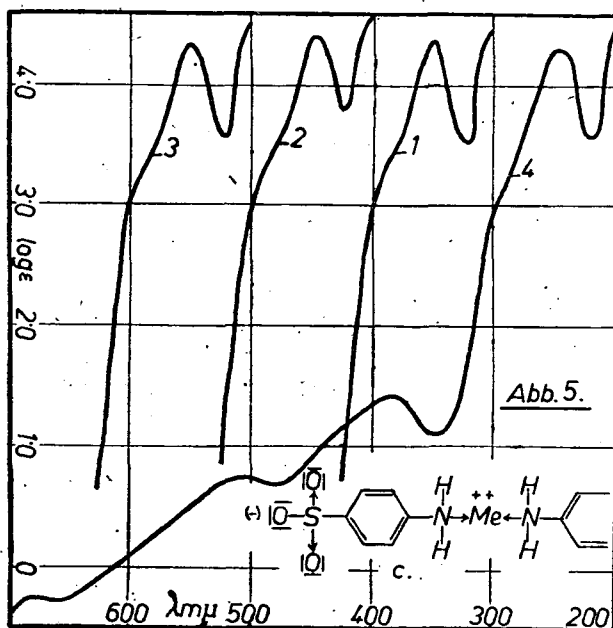


Abb. 5. Kurve 1: Cd-sulfanilat. K. 2: Pb-sulfanilat. K. 3: Zn-sulfanilat. K. 4: Co-sulfanilat. c: Betainartige Struktur des Sulfanilsäure-Komplexes.

Deformation des Zentralions und der Liganden verursacht werden (7).

Im Sichtbaren zeigen die Orthanilsäure-Komplexe der ungefärbten Ionen: Mg, Zn und Cd eine schwache Extinktion (Abb. 3, K. 4–6). Dies ist ein Zeichen der inneren Komplexbildung. Bei den entsprechenden Komplexen von Sulfanilsäure (Abb. 5, K. 1 und 3) fehlt diese Extinktion vollständig.

Laut Extinktionsmessungen haben Sulfanilsäure-Komplexe, der Behauptung von Pfeiffer (1) entsprechend, eine betainartige Struktur. Orthanilsäure bildet dagegen mit den komplexbildenden Metallionen, nicht wie Pfeiffer angenommen hat betainartige Komplexe, sondern innerkomplexe Verbindungen.

Zusammenfassung.

Die Extinktionskurven von Orthanil- und Sulfanilsäure und ihrer Komplexe wurden mit den ein-, zwei und dreiwertigen Metallionen ausgemessen.

Die Alkalimetallkomplexe beider Säuren dissoziieren in ihren wässrigen Lösungen.

Mg, Zn, Cd, Cu, Co, Ni und Fe bildet, der Behauptung von Pfeiffer entsprechend mit Sulfanilsäure betainartige Komplexe, mit Orthanilsäure dagegen innerkomplexe Salze.

In den Komplexen beider Säuren bleibt die selektive Absorption von Orthanil-, bzw. Sulfanilsäure beibehalten, aber ihre Extinktion wird von den gefärbten Metallionen spezifisch geändert.

Als ein Zeichen der wahren Komplexbildung haben Orthanilsäure-Komplexe der farblosen Metallionen: Mg, Zn, Cd an der Grenze des sichtbaren Gebietes eine schwache Extinktion. Demgegenüber sind die entsprechenden Sulfanilsäure-Komplexe in diesem Gebiet durchlässig.

Szeged (Ungarn) Dezember 1948.

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Abstracts of Lectures Delivered at the Meetings of the Chemical Division
of Hungarian Engineers Free Trade Union,

Szeged. (8. V. 1948 — 1. II. 1949).

Résumé des Lectures de la Division Chimique de L'Union des Ingénieurs
Hongrois à Szeged (8. V. 1949 — 1. II. 1949).

Sitzungsberichte der Fachorganisation Ungarischer Ingenieure in Szeged.
(8. V. 1948—1. II. 1949).

1. *E. Fenyő: Sciences naturelles et matérialisme dialectique.* L'auteur examine les découvertes de la physique moderne et de ses recherches il fait des conclusions philosophiques. De ses conclusions il découle que chaque fait nouveau de physique moderne fait ressortir les vérités de la philosophie matérialiste dialectique dans le sens élaboré par Marx—Engels—Lenin. Chaque fois que dans la mécanique de quanta, la théorie de la relativité, la physique de noyau atomique on a matérialisé les notions considérées comme des notions spiritualistes tels que: espace, temps, énergie. Ensuite l'auteur explique l'importance de la façon dialectique de penser pour les recherches dans la physique et sciences naturelles modernes.

2. *G. Fodor: Mutarotation in the sterol series.* Lecturer recorded a new series of compounds, i. e. dextrorotatory dibromides of cholesterol and of their derivatives. These formed under heating from the known laevorotatory stereoisomers. This rearrangement proved to be reversible leading to an equilibrium mixture from which both components could be isolated. Dextrorotatory dibromides are more soluble in organic solvents than their stereoisomers. This property could be used in case of acetyl cholesterol dibromide for a useful preparation of trans-dehydro-androsteron. The steric structure of the stereoisomers was intensively discussed. Cf. G. Fodor, Hung. Acta Chim., 1 fasc. 2., 1—10 pages.

3. *Z. Szabó: Stationary states and the enhancement of the yield.* The reaction of carbon and hydrogen has been investigated between 1100—2600° C. The concentration of methane, as function of the temperature shows a course, which can be composed asymmetrically from several fundamental reactions. At the lower temperatures reactions occurring between molecules prevail, at the higher temperatures atomic reactions are predominant.

The numerical valuation of experimental data permits the estimation of the constants of these atomic reactions. The yielded reaction heats and the activation energies agree with the theoretically assumed values.

This investigation points to a possibility having some practical importance. Setting in a stationary state instead of an equilibrium it yields a higher concentration than the equilibriumal one. Stationary states can occur also before the equilibrium, but only the stationary state behind the equilibrium raises the concentration of the new compound and contributes to the enhancement of the yield. Such stationary states do not arise under conditions leading usually to equilibrium, but they are consequences either or inlet of an extraordinary energy or of appearance of a new reaction.

4. *S. Reitzer: Organic Fluorine Compounds.* (Review).

5. *G. Wilhelm: Hydrogen fluoride in organic chemistry* (Review.) Lecturer reported about the function and the recent use of HF in organic chemical processes. He recorded the properties of HF, as well as the advantages and disadvantages of its use in chemical reactions. The catalytic effect of HF, showed to be useful in alkylation, acylation, polymerisation and some specific reactions. In

other cases it is present as an fluorinating agent. The investigation of J. H. Simons and R. E. McArthur reported (1947) the oxidation of aromatic hydrocarbons to phenols, by means of HF as catalyst. This new catalytical agent got a great importance in the organic chemical industry.

6. *L. Vargha: Studies in Furan Chemistry.* On treating p-toluenesulfonyl 2-acetobenzofuranoxime (V.) with methanol and ethanol, respectively, in addition to ammonium p-toluenesulfonate four different substances (A, B, C₁, C₂) were isolated. The same A (C₁₀H₈O₃) and B (C₉H₆O₂) were produced both in methyl- and ethylalcoholic mediums, but C₁, obtained from the methanolic reaction product (C₁₂H₁₄O₄), was found to be different from that of the ethanolic one (C₂, C₁₂H₁₈O₄). The constitution of A and B has been determined by various methods, which definitely established their identities as being 2-methyl-3-hydroxy-chromone (X) and 2-keto-coumaran (XIV), respectively. A probable explanation is given as to the mechanism of the conversion of V into X and XIV.

The constitution of C₁ and C₂ could not be definitely established. Based on analyses and on the fact, that their oximes (XV) could be transformed into X, they represent possibly 2-methyl-chromanone-3-dimethylacetal and diethylacetal (XVI), respectively.

7. *V. Bruckner: Ring closure of isoquinoline derivatives I.* Pfeiffer et al (J. prakt. Chem. (2) 154, 157 (1940)) obtained a compound from brazilin for which they assign structure 1-(2-hydroxy-4-methoxyphenyl)-3-methyl-6,7-dimethoxy-isoquinoline I. On attempting synthesis of I. by the method described by Bruckner and Fodor (Ber. 71, 541 (1938)) they obtained a compound which was not identical with the compound obtained from brazilin. Therefore Pfeiffer et al assigned to the synthetic product the structure 1-(2-hydroxy-4-methoxyphenyl)-3-methyl-7,8-dimethoxy-isoquinoline. Consequently, the synthetic product of Pfeiffer et al is I and not II, so that the structure of the product obtained from brazilin is still undetermined. The structure of a series of isoquinolines, synthesized by the lecturer, by Fodor, Krámlí and Kovács formulated by them as 6,7-dialkoxy-isoquinolines, which was not accepted unreservedly by Pfeiffer, has been similarly proved by degradation to metahemipinic acid resp. to hydrastinic acid. Cf. Bruckner, Fodor, Kovács and Kiss, J. Amer. Chem. Soc., 70, 2697 (1948).

8. *G. Fodor: On the Ring Closure of Isoquinoline Derivatives. II.* As a continuation of the lecture recorded above lecturer proved that the compound obtained by Pfeiffer et al from hematoxyline for which they assumed structure 1-(2-hydroxy-3,4-dimethoxyphenyl)-3-methyl-6,7-dimethoxy-isoquinoline (I) has still an unknown structure. (I) was namely synthesized by the lecturer and his cow and found to be not identical with Pfeiffer's product. Degradation of this synthetic product to metahemipinic acid supported structure I, therefore the compound of Pfeiffer from hematoxyline now became uncertain. Pfeiffer described a degradation product of this compound (from hematoxyline) and suggested for it structure 1-carboxy-3-methyl-6,7-dimethoxy isoquinoline (II). Lecturer and his cow synthesized II and found it to be different from Pfeiffer's product. The correctness of structure II for the synthetic product has been confirmed by degradation to metahemipinic acid. Thus, the compounds of Pfeiffer et al can not be isoquinoline derivatives, their structures remaining still to be settled. Cf. Fodor, Bruckner, Kiss and Kovács, J. Amer. Chem. Soc., 71, in the press.

9. *A. Kiss: The interpretation of the absorption spectrum of benzene derivatives on the base of the inductive and mesomeric effects*

In the first part lecturer treats the inductive and electromeric effect exerted by the substituents on the absorption spectrum of benzene. To elu-

cidate this problem, lecturer explains, on the base of photography taken in the Institute, the structure of the extinction curves of some typical benzene derivatives on the ground of a critical survey of the mesomeric structure. He emphasizes, that this method of interpretation can only be applied if it is possible to describe the electron distribution with mesomeric structures, but in the case of the formation of molecular orbitals this is no more satisfactory. The explanation is only correct if it is in agreement with the physical and chemical properties of the compounds and if the recent quantummechanical researches confirm the conclusions (See: A. Kiss: Magy. Chem. Lapja 3. 1948, 393).

10. E. Csetneky: *The resonance of the sulphogroup*. The lecture treated the results of the investigations on the resonance capability of the sulphogroup, in the cases of the following compounds: benzene sulphoacids and their derivatives and of some aromatic sulfoncompounds. It reported the results of the measurements of the absorption spectra of these compounds, which are as follows: when the sulpho group is connected with an aromatic compound, it is only resonance-capable, if an other resonance-capable group (e. g. $\text{—H}_2\text{N}$, —OH) is attached to the benzene ring, which draws the sulpho group into the resonance of the benzene ring. (Acta chem. physica Univ. Szeged 2 (1948) 30.)

11. J. Hyross: *On the absorption of nitro compounds*. The absorption spectrum gives an information on the change of energy between the ground and excited states. The substituents influence differently the two states having an inductive effect and π electron system of the molecule, and an influence on the formation of mesomeric structures. The structures of the extinction curves of the aromatic nitro compounds differ from the curves of other derivatives of benzene. Although NO_2 is unsaturated and is therefore a mesomery-capable group, it has only a mesomeric effect in the excited state. The curves have three bands which can be found in every nitrocompound very clearly except the strong effect of the solvent disturbs them. The band at $248 \text{ m}\mu$ proves the existence of the NO_2 chromophor. The p-derivatives have only two maxima, this fact is due to the effect of the p-position of NO_2 . (Acta chem. physica Univ. Szeged 2 (1948) 76).

12. A. Pál: *The history and development of kindling a fire and the evolution in match-manufacturing*. This essay is a historical survey, which begins with the age when the prehistoric man reached a certain level of intellect, when he tried and was able to make fire consciously, from several sources of fire available him from Nature. Later on the long way of evolution, man invented the effective ways of kindling a fire independently of Nature; he learned the tricks how to preserve and keep it alive; he invented the various instruments of making a fire and gradually he arrived to the Swedish safety match used today all over the world.

Due of the most important stations of human culture was the fact that man made use of fire and employed it for his own purposes. From this starting point this study leads us along the long course of development of kindling a fire and match-manufacturing.

13. G. Varsányi: *Berechnung der Extinktionskurven von Kobalt-(2)-chloridlösungen*. (Acta Chem. Phys. Szeged 2 (1949), im Druck.)

14. L. Csányi: *Determination of Chromate-Ion with Arsenite and Diphenylamine as Indicator*.

An accurate and widely applicable method is described for the determination of chromate-ion. Chromate-ion can be reduced by acid arsenite solution. The reaction is catalyzed by manganese-ion. The indication was made

with diphenylamine reversibly and catalyzed by potassium iodide. The acidified arsenious acid solution is very constant in strength.

The following solutions are necessary for this method:

1. Decinormal arsenite.
2. Catalyst solution. A common solution of 0,0210 g. of KJ and 0,0050 g. of MnSO_4 in 250 ml of water.
3. Indicator solution.

The procedure is as follows: Acidify the sample of the chromate solution with 5—6 ml cc. sulfuric acid and add distilled water to 50—60 ml. Add to the cooled sample 5 ml of catalyst solution and one drop of indicator solution. Let the arsenious acid run into the chromate solution from a buret just so long till the blue color changes to light green.

15. *L. Kalmár: A science applied without understanding it.* Both Mathematics and Natural Science have their basis in reality; this is what insures the applicability of the former to the latter. Though we see often that scientists apply mathematics without understanding it. For the deepening of the gap between mathematicians and scientists, the philosophical idealism is responsible in the first line, under the influence of which mathematics has been developed in a way as if it would have no connection with reality. In the second line, conservatism of the scientists is responsible too, for they prefer to apply mathematics in the form in which it first has been applied, e. g. mathematical analysis in the form before Cauchy's and Weierstrass's criticism, in which it is not to be understood at all. The only way of elimination of the gap in question is to re-formulate mathematics in a perspicuous way, in connection with reality, and to re-formulate science so as to apply in it mathematics re-formulated thus. This is a task of the revolutionary scholars of the Eastern European countries developing towards socialism.

16. *D. Kőszegi: Titrimetrische Bestimmung der Salpeter- und Schwefelsäure nebeneinander.* Nach dem Verfasser wird die volumetrische Bestimmung der Mischung die die beiden Säuren im freiem Zustande enthält, durch Titrieren von zwei Proben durchgeführt. (Die eingewogene Substanzmengen sollen möglichst nicht mehr als 0,2 g Gesamtsäure enthaltenen). Wenn wir die eine Lösung — nach dem Verjagen der zufällig absorbierten CO_2 — mit carbonatfreiem 0,1 n NaOH titrieren, bekommen wir die Summe der vorhandenen Salpeter- und Schwefelsäuremenge. Von der anderen Einwaage wird die Salpetersäure jodometrisch bestimmt, in der Weise, dass wir die eingewogene Säuremischung zu einer von 0,3—0,5 g Baryumcarbonat bereiteten wässrigen Suspension geben. Die Salpetersäure setzt eine äquivalente Menge Baryumnitrat frei, welches mit 0,1 n $\text{K}_2\text{Cr}_2\text{O}_7$ jodometrisch bestimmt werden kann. Der Unterschied der beiden Bestimmungen, gibt die Menge der Schwefelsäure.

17. *E. Vinkler: A new formation of 2, 3, 6, 7-tetramethoxythianthrene.* Lecturer found with J. Szabó, that — in order to prepare 3,4-dimethoxy-thiophenole — in presence of a little water zincdust reacts vigorously with veratrol-sulfonylchloride. By treating the reaction mixture with hydrochloric acid they could isolate near the thiol frequently large, but various amount of 2, 3, 6, 7-tetramethoxythianthrene of Fries. Beneath the reaction conditions of Fries the sulfonylchloride forms the thiol in a good yield. In order to identify the compound they have prepared the disulfoxyde- and disulfonederivative of 2, 3, 6, 7-tetramethoxythianthrene. (June 10 th 1948).

18. *I. Prettenhoffer: Improvement by machine of limeless soils.* In his lecture the author is dealing with the methods of the improvement of the limeless alkali soil covering about 400.000 cadastral acres of the Lowland. He

is writing about the chemical principals of the improvement and in what soil properties the improvement can be carried out by liming and when by spreading with a lime containing subsoil. Spreading has been carried on by hand for a 150 years. The improvement was not succesful everywhere because till now it has been done in a stereotyped manner and without taking the properties of the soil into consideration. On the grounds of the research work of the institute, after stating the conditions of favourable improvement, the possibility of improvement can be stated beforehand by the help of soil examination under such conditions the work could be started with greater mechanical strenght. The work has been in progress first with dragline and since 1947. with uptodate scrapers of great performance, with them it is possible daily to improve 8—10 cadastral acres of alkali soil. The result of improvement is permanent and the alkali soil, which bore 6—8 cwt of wheat per cadastral acre before improvement, bears 16—20 cwt after the improvement and on it nearly every useful plant can be grown with success.

19. Ö. Kovács und I. Kandel: *Über die Gerbung mit pflanzlichen Naturstoffen. (Zusammenfassender Bericht).*

20. I. Sarudi: *Dosage de l'acide phosphorique sous forme de phosphomolybdate d'ammonium.* L'auteur dose le phosphore contenu dans des produits complexes sous forme de $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ de façon que le précipité molybdénique qui était obtenu par deux précipitations successives, est posé après séchage à 160° . D'après les données de ces recherches la valeur trouvée calculée en P_2O_5 est de 3,772%, qui ne diffère que de peu de la quantité théorique 3,783%. Il démontre l'exactitude de sa méthode par des dosages effectués sur des solutions de phosphates pures de même que par des dosages sur des apatites et pyromorphites.

21. É. Salgó: *Über die massanalytische Bestimmung von Theobromin und Theophyllin.* (Gemeinsame Arbeit mit D. Kőszegi). Theophyllin und Theobromin lassen sich mit der Hilfe des $\text{K}_2\text{Hg}(\text{SCN})_4$ quantitative bestimmen. Wenn man diese Verbindungen mit $n/10$ NaOH-Lösung zu ihren Natriumsalzen umwandelt und mit $n/10$ $\text{K}_2\text{Hg}(\text{SCN})_4$ -Lösung behandelt, entstehen die Mercurisalze: $(\text{Theophyllin})_2\text{Hg}$, bzw. $(\text{Theobromin})_2\text{Hg}$, und wird gleichzeitig Rhodan in äquivalenter Menge frei. Nun wird die niederschlaghaltige Lösung durch 20 Minuten vorsichtig erhitzt, filtriert und in dem aliquoten Teil des Filtrats das freigewordene Rhodan mit $n/10$ AgNO_3 -Lösung abgeschieden. Der Überschuss de AgNO_3 wird in salpetersäurigem Medium, in Gegenwart von Ferrisalz mit $n/10$ KSCN titriert. Als Vorteil der Methode ist zu erwähnen, dass die genannten Purinbasen sich auch neben dem Coffein abscheiden lassen, da das Coffein mit dem $\text{K}_2\text{Hg}(\text{SCN})_4$ nicht reagiert.

22. Z. Csűrös: *Catalyse sélective.*

23. Z. Szabó: *The Catalytic Effect of Metals of Changing Valency on the Corrosion.* An increasing concentration of cupric ion accelerates the corrosion so that $\log(\text{Cu}^{++})$ is a linear function of time, which points to a first order reaction relating to the cupric concentration. The present halogene ions exert an especially strong accelerating effect. The corrosion increases with increasing H-concentration.

The stirring is without influence on the corrosion velocity, which points to the fact that the process determining the velocity is a reaction which does not occur on the phase surface.

The reaction rate can only be controlled by the process: $2\text{Cu}^{++} + 2\text{H}^+ + 1/2\text{O}_2 = 2\text{Cu}^+ + \text{H}_2\text{O}$. So we obtain an equation for the corrosion, in which $[\text{Cu}^{++}]$ is on the first power, and the influences of H^+ and Cl^- ions can also be taken into account.

The catalyzing effect of the halogene ions are based on the formation of complex ions, by which the Cu activity is still considerably more lowered, than in the case of oxidation. Thus the equation of the reaction rate, of the corrosion speed will be:

$$-\frac{d[\text{Cu}]}{dt} = k_1 [\text{Cu}^{++}] [\text{H}^+]^2 [\text{O}_2]^{1/2} \quad \text{resp.} \quad -\frac{d[\text{Cu}]}{dt} = k_2 [\text{Cu}^{++}] [\text{H}^+]^2 \frac{[\text{Cl}']^6}{K_2^2} [\text{O}_2]^{1/2}$$

where K_2 is the complex constant.

24. C. Kell: *Modern dewaxing methods*. Recitator gives a short description of the theories and apparatus of the classical dewaxing methods and gives their comparison, with modern processes, known under the names of A. B. T., Barisol, Propan, Dr. Kell etc. methods. He renders prominent the Dr. Kell and the Propan processes, as of such kind, with which you have the possibility for dewaxing directly residues and the mentions also, that the Dr. Kell process can select the naphthenic oil parts, from the paraffinic oils during the dewaxing, without using peculiar apparatus for doing that. He speaks also on the solvents used in the processes and enumerates the advantages and the disadvantages of each process.

25. L. Kalmár: *Dialectical features of Mathematics*. Some mathematicians do not feel well unless they can work within exactly defined frames; everything outside their actually accepted frames they feel „vague.“ Other mathematicians are convinced that exactly defined frames are always too narrow. These views correspond to dogmatical and dialectical philosophy, respectively. Irrational numbers, geometrical construction problems unsolvable by ruler and compass, algebraic equations unsolvable by the four first rules and root extraction, integrals which cannot be expressed by elementary functions, etc., are symptoms of the right of dialectical mathematicians. Set theory has shown that such symptoms are not exceptional as one first supposed, in the contrary, in most cases they form the rule and the entities fitting into the frames are exceptional. Recent results in mathematical logic (of Tarski, Gödel, Church) furnish general theorems showing that exactly prescribed frames are necessarily too narrow to catch the reality, even in mathematical field. This is a strong argument for dialectical philosophy.

26. A. Lózsá: *Zur gegenseitigen Beeinflussung chromophorer Gruppen*.

28. L. Mészáros: *Methoden zur Konservierung von Lebensmitteln*. (Review).

29. P. Simonffy: *Syntheses of Butadien*. (Review).

30. T. Geréb: *Dialectical scientific thought*. True scientific thought was always dialectic and — at least in the sphere of the special branches of the scientist — materialistic. Marx and Engels united dialectics with materialism based on contemporary natural science. Dialectic trend of thought regards the laws of nature as unilateral relations of the complex connections of nature; for the dialectical scientist law of nature has no absolute validity, divergencies between experience and law are foreseen by him and explained by further causal factors. Dialectics, contrary to conditionalism, do not only take into consideration the conditions, the constellation and interaction of conditions but also the reaction of the explored phenomenon on the conditions. Human mind can only comprehend relations arbitrarily deprived of its connections, abstract metaphysical trend of thought is therefore a necessary aspect of thought, but only as a transitory stage of dialectical thought. Truth and error in science are not irreconcilable contradictions, truth has also its relative, temporary, unilateral aspects, error on the other hand is a one-sided exaggeration of some relative truth. Contradictory scientific statements reflect inner contradictions of reality, emphasising opposite sides of reality. History of science developed in

scientific periodicals reflects this truth far better than the intentionally simplified mode of treatment of textbooks.

31. I. Kiss: *Molecular distillation*. (Review).

32. R. Balló: *Plastics*. (Review).

33. A. Kiss: *On the effects hindering mesomerism*. The only correct interpretation of the extinction curve of the aromatic compounds can be given by taking the following facts into consideration:

the reciprocal effect of the mesomeric and inductive effects;

the effect hindering or promoting mesomerism, the groups of identical or contrasting character in o-, or p- positions;

the effect hindering mesomerism of the group in m- position;

the steric hindrance;

He elucidates the mentioned affects using spectrophotometrical measurements taken in the Institute. (See details: A. Kiss and E. Csetneky: *Acta chem. physica Univ. Szeged.* 2 (1948) 30, 37, 132. A. Kiss, G. Fodor and A. Lózsza: *Acta chem. phys. Univ. Szeged* 2 (1948) 25. A. Kiss and R. Pauntz: *Acta chem. physica Univ.* 2 (1948) 83.

34. I. Kovács: *Dialectics in modern physics*. The lecturer exerted to elucidate the decisive part of main principles of dialectics in the development of modern physics. So at first he demonstrates that the initiation of the category of changes through jump into physics, fully changed the direction of development of modern physics (quantumtheory); he illustrated with examples the transition of quantitative changes into qualitative changes (periodical system, chemistry). He compares the „eternally unchanged“ world of classical physics with the processes of change, development transformation, origination and annihilation of modern physics (radioactivity, transmutation of elements). He explained the main lines of development through contrasts, just as how the each other exclusive contrast became each other suppositional, each other supplementary dialectical contrasts the double character of light and corpuscular radiation). At least he establishes, that how does the right recognition of the principle of coherence lead to important principal significative statement, which transformed our physical thinking (the coherence between measuring instrument and system to measure; the relation of Heisenberg).

35. J. Kiss: *The stereochemistry of 4-hydroxy-3-methoxy nor ephedrine*. Two 4-hydroxy-3-methoxy-phenylpropanolamines formed from two different psi-nitrosites on synthesizing in an essentially identical manner, they showed various physical constants. To determine this difference lecturer, Fodor and Szerkerke investigated the connection between the derivatives obtained from both psi-nitrosites; furthermore by the method of isonitroso-kefones the suitable other diastereoisomer was synthesized. Based on the literature data the later synthesis favours in all cases the formation of an ephedrine structure. The compound synthesized in this manner was not identical with any of the previous isomers. They established that by one of the acetylated products, synthesized by route of psi-nitrosite, under acid hydrolysis a change of configuration took place, so that one of the endproducts was not a unitary compound, but a molecular compound of the two diastereoisomeric pairs, showing a constant mp. Therefore the psi-nitrosite synthesis in the cases described above also led to a structure of psi-ephedrine, which was no exception on the general rule established in the course of the institutes work. Cf. Fodor, Kiss and Szerkerke, (*J. org. Chem.* 14 (1949) in the press).

36. E. Fenyő: *Mathématique et marxisme*. Les récents développements des sciences mathématiques ont produit des résultats très importants quant à leurs conséquences philosophiques. La théorie de logique mathématique bien connue

de Gödel démontre l'impossibilité de soutenir la thèse de l'objectivisme logique. Ceci en effet démontre que dans chaque système logique il existe des problèmes qui sont impossible à résoudre dans ce système fermé. Cela veut dire que la façon de penser antidialectique plutôt dogmatique amène irrévocablement à l'agnosticisme de telle sorte on doit le considérer comme un système incapable à expliquer l'univers. D'un autre point de vue les mathématiques sont fondamentement matérialistes puisque d'après un des annoncés de Skolen on peut considérer que plusieurs des conceptions de mathématiques comme par exp. les nombres irrationnels ne peuvent être compris autrement que comme des abstractions des faits matérialistes. L'auteur a analysé en quoi consiste l'intuitionisme mathématique et il a trouvé que les conséquences philosophiques de cette dernier sont les mêmes que les conclusions de l'Hilbertisme. D'autre part il est clair qu'on peut considérer le système intuitioniste de Brouwer comme le pendant mathématique de l'intuitionisme philosophique de Bergson. Comme conclusion: les deux écoles extrémistes de philosophie bourgeoise: l'objectivisme rationaliste et le mystique irrationnel en somme disent la même chose et leur combat n'est qu'une lutte de don Quichotte.

37. L. Kálmán: *The Establishment of the Mechanism of Catalytic Reactions Based on Experimental Data*. The establishment of the reaction mechanism usually occurs by the measurement of the reaction rate and the reaction order, which can be determined from it. In the case of complex processes, however, the rate of the simultaneous and consecutive reactions cannot be measured so that this reaction mechanism cannot be established. In such cases the establishment of the reaction mechanism can be done in the following manner: 1. The establishment of the theoretically presumable reactions and mechanism from the data of the analysis. 2. The exclusion of the unlikely kinetic and thermochemical reactions. 3. The justification of the assumed reaction course calculated by the examination data of volume and percentage obtained from the data of the analysis. The given calculation method involves the simplest mathematical calculations and is based on the gas laws, so that it can be easily and widely employed in cases in which other methods are not efficient.

38. I. Back: *Über die Forschungsprobleme der ungarischen Farbstoffindustrie*. (Zusammenfassender Bericht).

39. I. Marton: *The 2 years of the Hungarian dyestuff manufacture*. Reporter lectured on the circumstances, when the Hungarian dyestuff-manufacture started, on its program and on the 2 years experiences. The first step was the rebuilt of some war-plants, to cover the remarkable dyestuff need appearing after the country's deliberation. The principal problem was the building of pilot-plants. During these 2 years, 26 dyestuff-species were manufactured, which weighed 300 tons amounting to abt. 10,000,000.— Ft. The actual manufacture's capacity covers ab 20% of the home-need; at the same time an export started too. The principal manufacture's lines are: sulfur dyes, chromic wood dyes, Nigrosines, as well as some acid-, direct- and lake-dyes. The preliminary plan for 1949 is to manufacture 350 tons of 34 dyestuff-sorts, amounting to 16,000,000.— Ft. This new-industry is a very important one, especially as regards the development of the Hungarian organic-chemical heavy industry.

40. A. Lőrinc: *Actual problems of the Hungarian dyestuff manufacture*. The 3 principal phases of the aniline-dyestuff manufacture are: 1. research, 2. the manufacturing itself, 3. colouring. The expression „colouring“ indicates the chemical and technical operations in the textilefinishing-, leather-, paper- and chemical industry, aiming the permanent colouring of goods, based on scientific methods. The colouring can be a general one, that is the dyeing and local colouring; in this case we speak of printing. Local colouring in the leather-and

chemical-industry is unusual. The dyestuff industry in general, or a dyestuff factory can be prosperous only in case of an intensive cooperation with his own colourist as well as with the manufacturing industry's colourists. The real appearing of the colouring is the textile printing, when the colours are placed harmonious side by side in a way, that the different colourgroups do not trouble each other even chemically. The Hungarian dyestuff industry's essential interest is not only to increase the employment's possibilities in our country, but to improve their quality, enabling to compete with the foreign countries, products. That is the point on which the export problem is connected with our dyestuff manufacturing program.

41. *E. Obermayer: Growing cotton in Hungary.* Lecturer states the cotton to be the most important textile raw material of mankind. As Hungary has a great import of cotton, it seems desirable to secure this requirement at least partly by inland production. Cotton growing on the northern hemisphere is generally limited to the 40th grade of northern latitude. The fact, that Hungary lies between the 46th and 48th grades and consequently the growing season is shortened, the mean temperature too low, the quantity of warmth and sunshine reduced, makes here the cotton cultivation especially difficult. Several unsuccessful experiments in cotton growing have been made in Hungary since 165 years. This failure can easily be understood now as the varieties used were always belonging to late maturing types. As shown by recent experiments performed in the Plant Breeding Institute at Szeged, the Upland varieties of shorter growing period brought up to young plants in warm bed give a very sufficient yield. These varieties if made more early by proper breeding and grown under special agrotechnical circumstances determined by the experiment, institute above mentioned may be grown profitably even by sowing directly on the field. In this way in a normal year in the warmer areas of the country it will be possible to approximate the average yield of the foreign cotton growing lands. Since our cotton-fibre proved suitable for industrial purposes we will start a greater breeding work in spring 1949.

42. *Gy. Bácskai: Oxidation and corrosion.* The lecture explains the development of the oxidfilms on the surface of the metals and their role in the corrosion. It describes the mechanism of oxidation of the metals and alloys, separately in the case of the light respectively heavy metals. It reports on the methods, which renders possible the separation of the oxidfilm from the metal-surface and its examination. It touches briefly on the essence of corrosion, illustrating by experiments, the difference between the corrosion of the metal-surfaces protected and not protected by oxidfilm. Finally it states the corrosion investigations on the artificially produced oxidprotectedfilm.

43. *Z. Szabó: Transurans, Urans and the Periodic Table.* Seaborg and Wahl have recently published an article of the chemical properties of elements 94 and 93, indicating that the transuranc elements are members of a group of atoms similar to the rare earths. Calculations concerning the arrangement of electron shells indicate the starting of a new rare earths group at the elements 91 or 92. Investigation and comparison of the physical (the monotonous changes of the specific weights and of the melting points) and chemical properties (the variation of the ionization potentials and the electrochemical behavior) in relation to the periodic system support the opinion that the new group should be started with Actinium because the physical and chemical properties of the elements (Ac, Th, Pa, U, Np, Pu) fit into the character of the III. column.

44. *P. Benedek: Neuere Ergebnisse der Acetylenchemie.* (Vgl. Magy. Kém. Lapja, 4, (1949), 1, 72.)

45. *F. B. Straub: The role of adenosinetriphosphate in muscle contraction.*

The analysis of actin (a protein taking part in muscle contraction) has revealed the presence of bound Ca and bound adenosinetriphosphate. When salts are added to actin, it changes from a globular protein into a fibrous modification. During this change of form, the adenosinetriphosphate in it changes into adenosinediphosphate. This reaction is not due to an adenosinetriphosphate action. Adenosinetriphosphate has strong positive inotropic action on the isolated frog's heart. It is suggested that the polymerisation of actin is connected with the processes of muscle contraction and the known effect of adenosinetriphosphate in model systems is connected with the changes in actin-bound adenosinetriphosphate.

45. G. Fodor: *A newer method for the separation of diastereoisomeric amino alcohols*. (12. XII. 1948.) In continuation of a work on diastereoisomeric amino alcohols (cf. J. org. Chem. 14, May 1949.) a newer method for the separation of this type of compounds using acyl migration $N \rightarrow O$ was investigated. Lecturer gave first a survey of acyl migration reactions and then treated the new method in detail. N-Carbobenzoxy-dl-nor-ephedrine and N-carbobenzoxy-dl-nor- ψ -ephedrine could be isolated by treating their mixture with alcoholic hydrogen chloride. The water insoluble ephedrine derivative was recovered unchanged, whereas the ψ -ephedrine derivative underwent acyl migration yielding O-carbobenzoxy dl-nor- ψ -ephedrine hydrochloride, which is easily soluble in water. Each separated carbobenzoxy derivative was then hydrogenated catalytically, and furnished the corresponding amino alcohol besides toluene and CO_2 (Cf. Fodor and Kiss, Nature, (1949) 287). This behaviour is a consequence of the relative steric positions of acylamido and of the hydroxyl groups. In the ephedrine series, however, the method could not be used for the decision of the configuration. On the contrary, in the series of isocyclic amino alcohols, e. g. 2-amino cyclohexanol, occurrence, or failure of acyl migration reaction surely proves „cis“ or „trans“ configuration. At the Institute of Organic Chemistry lecturer and Dr. J. Kiss carried out experiments to decide the still unproved configurations of the diastereoisomeric 2-amino-cyclohexanols, using their benzoyl and carbobenzoxy derivatives.

